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16. ABSTRACT The report gives results of a theoretical investigation of the disposition of five volatile trace elements (arsenic, boron, lead, selenium, and mercury) in SNG-producing coal gasification plants. Three coal gasification processes (dry-bottom Lurgi, Koppers-Totzek, and HYGAS) were investigated to examine the possible effects of gasifier operation conditions on the speciation of the volatile trace elements. The dispositions of these volatile trace elements in a general gas processing scheme (consisting of gas quench, acid-gas removal, and combined shift methanation) were then projected. A different acid-gas removal process was used in each process: the Rectisol process was used for the Lurgi projection; the Benfield, for the Koppers-Totzek; and the Selexol, for the HYGAS. Results of this investigation suggest that none of the trace elements considered in this study will be present in the product SNG from a coal gasification plant, but will be removed from the fuel gas by various unit operations. Results also suggest that speciation of these volatile trace elements is not significantly affected by gasifier conditions.

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THEORETICAL INVESTIGATION OF SELECTED TRACE ELEMENTS IN COAL GASIFICATION PLANTS

by

A. H. Hill
G. L. Anderson
D. K. Fleming

The Institute of Gas Technology
3424 South State Street
Chicago, Illinois 60616

Contract No.: 68-02-2648

Project Officer

William J. Rhodes
Gasification and Indirect Liquefaction Branch
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF ENVIRONMENTAL ENGINEERING AND TECHNOLOGY
OFFICE OF RESEARCH AND DEVELOPMENT
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ABSTRACT

As a preliminary effort in determining the extent to which trace elements may persist in quenched raw product gas streams in coal gasification processes, this theoretical investigation was initiated. Five trace elements were selected based on their reported volatility in process development units (PDU), pilot plant operations, or commercial-scale operations. These are arsenic, selenium, boron, lead, and mercury. Three distinct coal gasification technologies were selected to investigate the possible effect of gasifier operating conditions on volatile trace-element compound formation. The technologies chosen were the non-slagging Lurgi, the Koppers-Totzek, and the HYGAS process.

Models were developed based on available literature data on the behavior of the trace elements in question under conditions similar to those expected in coal gasification processes. Much of the data, particularly kinetic data, needed to develop accurate models of trace element behavior are not available, and, in most cases, assumptions based on kinetic theory were necessary.

The significant conclusions that can be drawn from these data for the five elements selected for this study are as follows:

- Arsenic volatilization from coal does not appear to be significant until gasification temperatures exceed 1000 K (1341°F). Part of the arsenic volatilized appears to be absorbed or condensed on the char in cooler sections but is not sufficient to reduce losses to less than about 50%.

- Boron appears to be removed from the coal at relatively low temperatures (<750 K, 891°F). Further volatilization appears to occur at higher temperatures but is retained in the char by absorption or condensation on chars in a cooler section (second stage) of the gasifier.

- Selenium does not appear to be volatilized from the char until temperatures in excess of 1000 K (1341°F) are reached. Little, if any, absorption of the volatilized selenium seems to occur in the cooler sections.

- Lead volatilization begins at temperatures in excess of 1000 K (1341°F) but appears to be nearly quantitatively retained by the chars by condensation or absorption on chars in the cooler stages.

- Mercury is volatilized from the coal at temperatures less than 750 K, (891°F).

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1. INTRODUCTION

Many coal gasification processes to produce substitute natural gas (SNG) are either available or under development. Deployment of this technology to supplement the available supply of natural gas is expected to accelerate in the United States in the next several years.

The U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy (DOE) have supported a number of programs to determine the potential environmental impact of this technology. The disposition of trace elements in the coal gasification process has been the subject of many of these programs.[1-4] The results of these studies indicate that most of the trace elements remain with the residue. A few of the elements, however, appear to be quite volatile and leave the coal to be disposed of in downstream operations. In most studies, these volatile trace elements have been assumed to be disposed of in one or more of the condensate streams derived from primary gas quenching operations. However, a number of inorganic compounds such as arsine (AsH_3), hydrogen selenide (H_2Se), mercury (Hg), and boron hydride (BH_3) are quite volatile at ambient conditions and may pass through the quench system unhindered. Without knowledge of the possible presence of these "volatile" trace elements in the quenched gas stream, emission of these trace elements into the environment may take place.

As a preliminary effort in determining the extent to which trace elements may persist in quenched raw product gas streams in coal gasification processes, this theoretical investigation was initiated. Five trace elements were selected based on their reported volatility in process development units (PDU), pilot plant operations, or commercial-scale operations. These are arsenic, selenium, boron, lead, and mercury. Three distinct coal gasification technologies were selected to investigate the possible effect of gasifier operating conditions on volatile trace-element compound formation. The technologies chosen were the non-slagging Lurgi, the Koppers-Totzek, and the HYGAS process.

2. BACKGROUND

2.1. The Gasification Process

Numerous technologies exist for gasifying coal, yet the basic chemistry involved in most of the technologies is similar. Coal is reacted with steam and oxygen under fuel-rich conditions and elevated temperatures to produce a fuel gas containing primarily hydrogen, carbon monoxide, carbon dioxide, methane, and unreacted steam. The major difference between gasification technologies is in the operating conditions. Figure 1 illustrates the large variation in operating conditions that exists among the many coal conversion technologies.

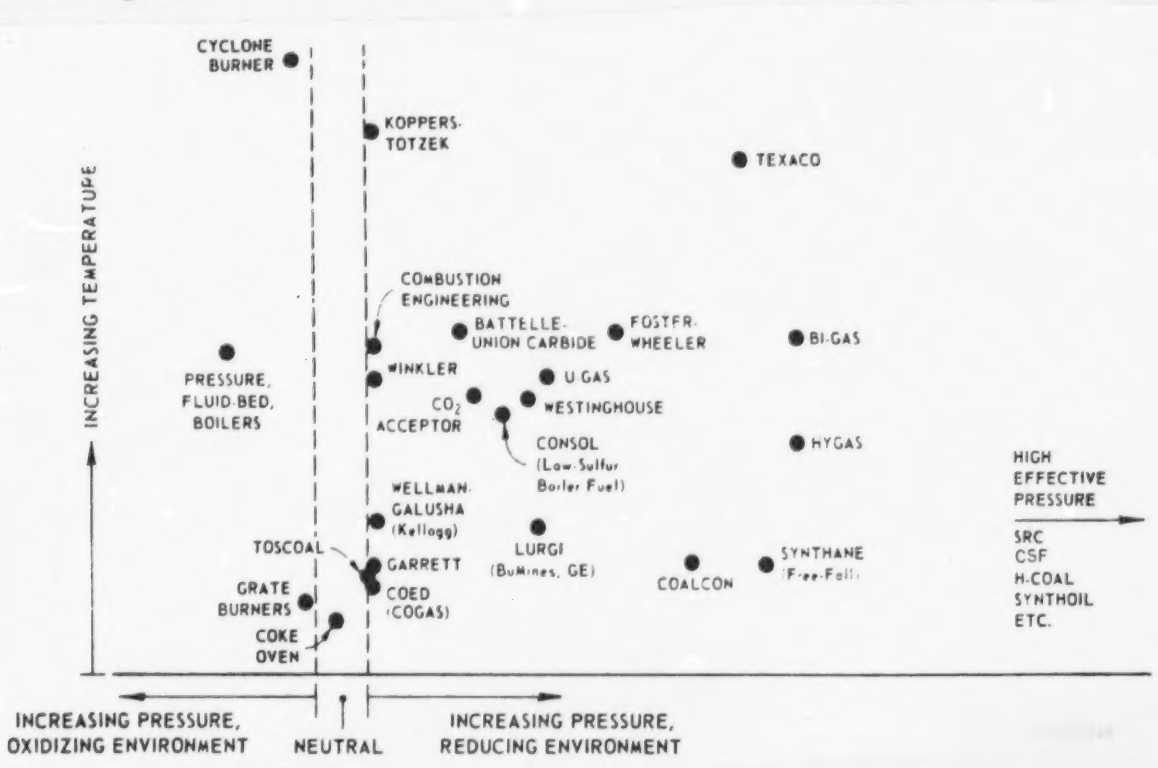

Figure 1. Comparison of fuel conversion processes.

These variations in operating conditions might have a large impact on the extent of formation and the product distribution of volatile trace-element-containing compounds. As mentioned previously, three distinct gasification

technologies were chosen to examine this effect. A brief description of each of these processes is given below.

2.1.1. Koppers-Totzek Process

In this process, pulverized coal is reacted at low pressure and high temperatures (>1800 K, 2780°F) with steam and oxygen in an entrained bed with cocurrent gas/solids contacting. A simplified diagram of the gasifier is shown in Figure 2. The high gasification temperature assures nearly complete gasification of the carbon in the feed coal. Approximately 50% of the ash in the coal flows down the gasifier walls as molten slag and drains into a slag quench tank. The remainder of the ash leaves the gasifier as fine particles entrained in the exit gas. These particles are solidified at the gasifier exit by water sprays and are subsequently separated from the scrubber water and disposed of with the solidified slag.

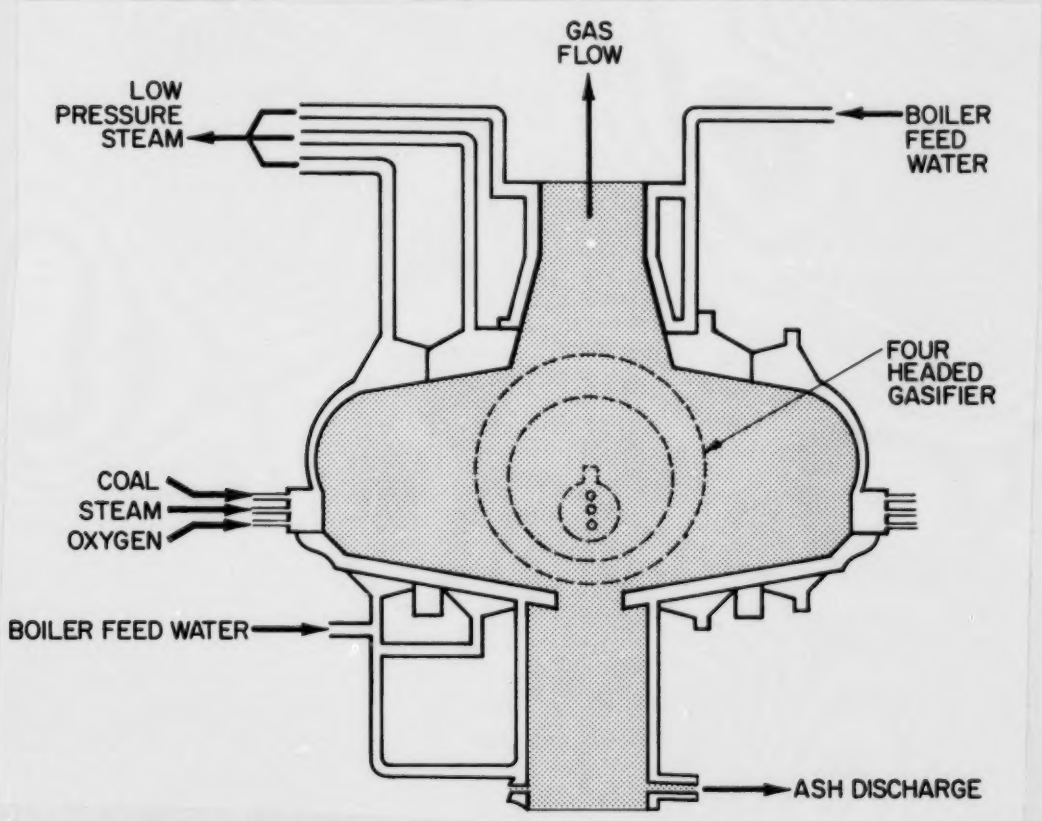

Figure 2. Koppers-Totzek gasifier.

The high operating temperature and low operating pressure of this process produces a raw product gas from the gasifier primarily composed of H_2, CO, CO_2, and steam with minimal amounts of hydrocarbons and tars.

2.1.2. Lurgi Process

The Lurgi process employs a gravitating bed of coal with continuous countercurrent gas flow as shown in Figure 3. Coal is fed intermittently to the top of the reactor through pressurized lockhoppers, while oxygen and steam are mixed and fed into the bottom of the gravitating coal bed. Gas temperature ranges from 590 K (603°F) at the top of the gasifier to 1260 K (1809°F) at the bottom of the gasifier. Normal operating pressures are 2.03 to 3.24 MPa (20 to 32 atmospheres), and coal residence time is approximately 1 hour. These operating conditions produce a change in the product gas composition from that produced by the Koppers-Totzek process. Roughly 19% of the feed carbon reacts to form methane and ethane rather than carbon oxides, and approximately 12% of the feed carbon is converted to tar, fatty acids, phenols, and benzene, toluene, xylene (BTX).

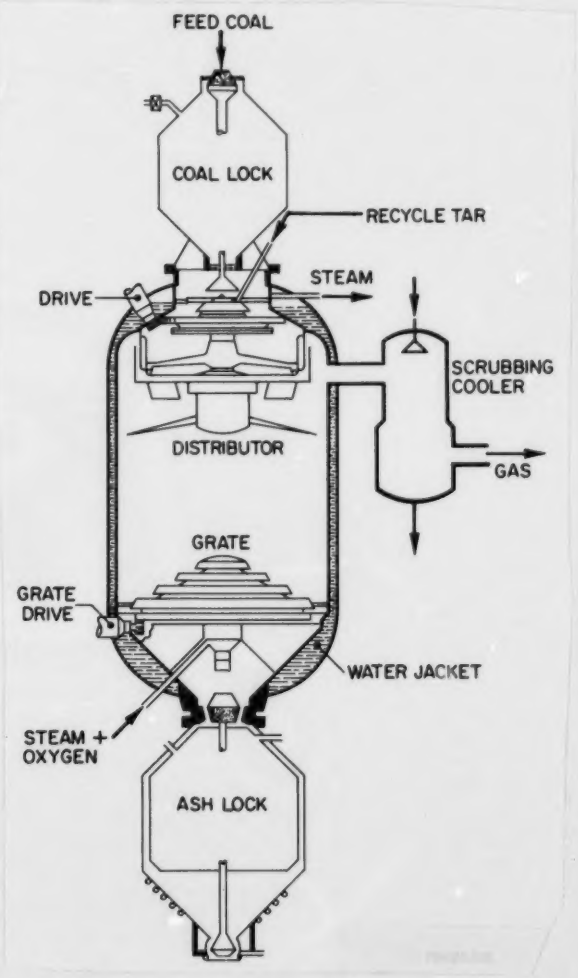

Figure 3. Lurgi pressure gasifier.

2.1.3. HYGAS Process

The HYGAS process uses three separate reaction stages for gasifying coal. A diagram of the gasifier is shown in Figure 4. Coal is fed to the gasifier as a slurry made with either aromatic oil or water. The oil or water is vaporized in a fluidized bed (the slurry dryer) in the top of the gasifier using heat available in the product gas from the top reaction stage. The dried coal is then gravity fed to the first stage, entrained, and reacted in a low-temperature reactor stage (LTR) with product gas from the lower sections of the reactor. The operating temperature for this section of the gasifier is normally between 920 and 1060 K (1197° and 1489°F). The reacted coal from the first stage is then disengaged from the gases and gravity fed to the fluidized-bed second-stage hydrogasifier where it is reacted with product gas from the lowest stage of the gasifier at temperatures between 1030 and 1170 K (1435° and 1647°F). Finally, the reacted coal from the second stage is gravity fed to the lowest stage of the gasifier, the SOG (steam-oxygen gasifier), where the remaining carbon in the coal is reacted with high-pressure steam and oxygen at temperatures between 1170 and 1280 K (1647° and 1845°F). The normal operating pressure of the HYGAS process is 6.99 to 10.1 MPa (69 to 100 atmospheres). In this process, methane and ethane account for 27% of the feed carbon while 8% or less of the feed carbon produces BTX and phenol. The production of tars and fatty acids by this process appears to be minimal.

2.2. Review of Reported Data on Trace Element Behavior in Gasifiers

Although a number of trace-element-disposition studies have been performed on gasification processes, the chemical forms of the trace elements volatilized from the coal have not been determined. However, the qualitative behavior of the elements can be deduced from published results.

A summary of findings from PDU-scale, pilot-scale, and commercial-scale gasification studies is presented in Table 1 for the five trace elements selected for this study. The losses reported in Table 1 were all based on differences in the concentration of the individual element in the feed coal with respect to the gasified char. The major assumption in these calculations is that the majority of the ash is retained in the gasified char. With this assumption, the loss of a particular element from the coal during gasification is computed by the expression —

$$\% \text{ loss} = \left(1 - \frac{C_c A_c}{C_f A_f}\right) \times 100 \qquad (1)$$

where —

C_c = concentration of the element in the product char, ppmw*
A_c = concentration of ash in the product char, wt %
C_f = concentration of the element in the feed coal, ppmw
A_f = concentration of ash in the feed coal, wt %

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* ppmw means parts per million by weight.

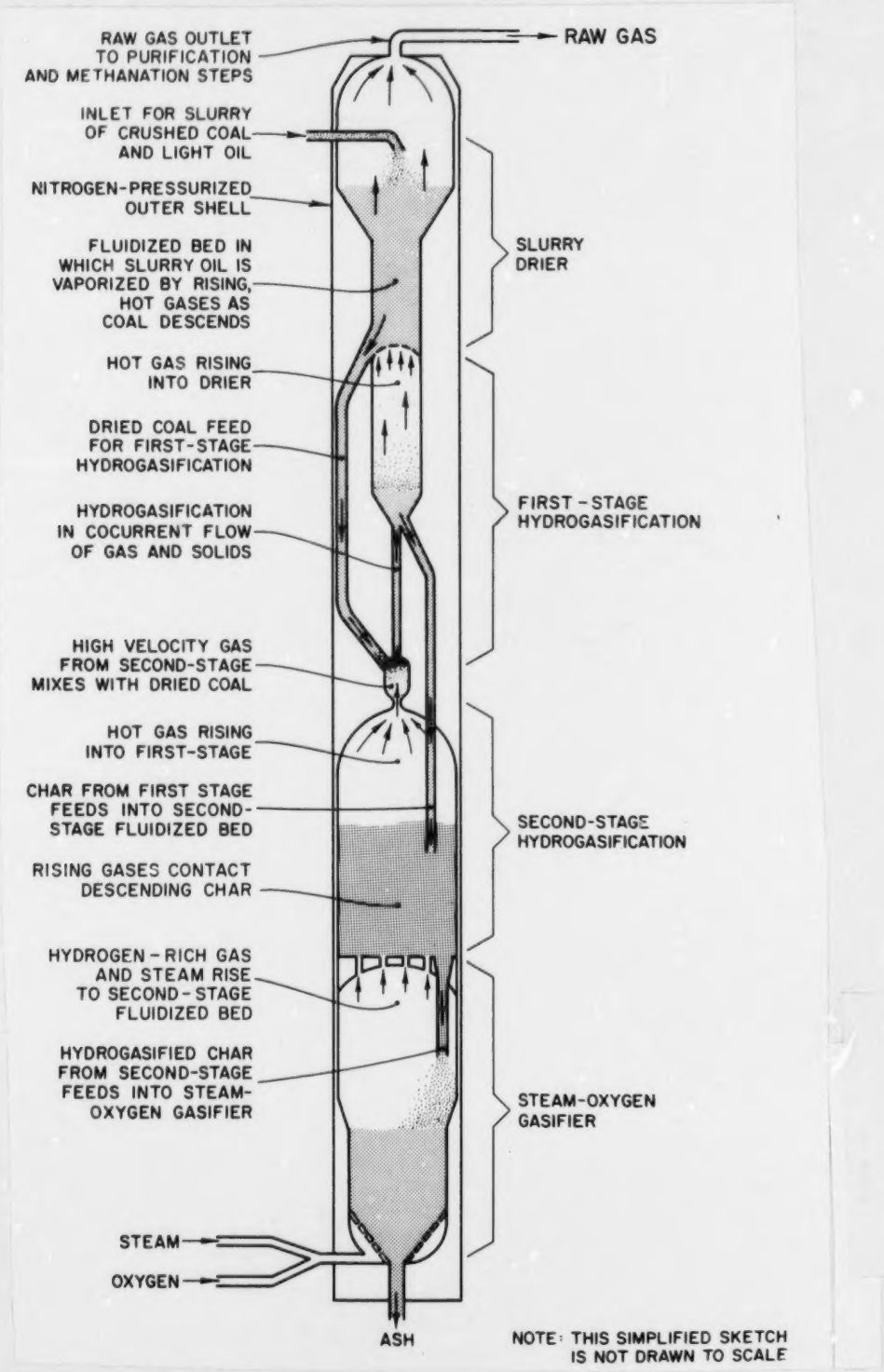
RAW GAS OUTLET TO PURIFICATION AND METHANATION STEPS
RAW GAS
INLET FOR SLURRY OF CRUSHED COAL AND LIGHT OIL
NITROGEN-PRESSURIZED OUTER SHELL
FLUIDIZED BED IN WHICH SLURRY OIL IS VAPORIZED BY RISING, HOT GASES AS COAL DESCENDS
SLURRY DRIER
HOT GAS RISING INTO DRIER
DRIED COAL FEED FOR FIRST-STAGE HYDROGASIFICATION
HYDROGASIFICATION IN COCURRENT FLOW OF GAS AND SOLIDS
FIRST-STAGE HYDROGASIFICATION
HIGH VELOCITY GAS FROM SECOND-STAGE MIXES WITH DRIED COAL
HOT GAS RISING INTO FIRST-STAGE
CHAR FROM FIRST STAGE FEEDS INTO SECOND-STAGE FLUIDIZED BED
SECOND-STAGE HYDROGASIFICATION
RISING GASES CONTACT DESCENDING CHAR
HYDROGEN-RICH GAS AND STEAM RISE TO SECOND-STAGE FLUIDIZED BED
HYDROGASIFIED CHAR FROM SECOND-STAGE FEEDS INTO STEAM-OXYGEN GASIFIER
STEAM-OXYGEN GASIFIER
STEAM
OXYGEN
ASH
NOTE: THIS SIMPLIFIED SKETCH IS NOT DRAWN TO SCALE

Figure 4. HYGAS pilot plant gasifier with steam-oxygen gasification.

TABLE 1. TRACE ELEMENT LOSSES FROM COAL DURING GASIFICATION OPERATIONS

Gasifier (Coal Feed)	As		B		Pb		Hg		Se	
	ppmw* in feed coal						(% loss)			
HYGAS PDU[1] (Ill. No. 6)	24	(33)	200	(10)	11	(47)	0.12	(96)	13	(42)
HYGAS PDU[1] (Mont. Lignite)	18	(52)	85	(28)	1.9	(47)	0.73	(99)	1.7	(66)
HYGAS Pilot Plant[2] (Rosebud Subbituminous)	0.5	(46)	80	(41)	5	(0)	0.02	(83)	0.4	(84)
HYGAS Pilot Plant[2] (Rosebud Subbituminous)	NA**	NA	80	(23)	5	(5)	0.02	(96)	NA	NA
Synthane PDU[3] (Ill. No. 6)	0.87	(4)	86	(37)	0.55	(0)	NA	NA	2.2	(3)
Synthane PDU[3] (Ill. No. 6)	0.87	(12)	86	(68)	0.55	(2)	0.10	(79)	2.2	(23)
Lurgi-Sasol Plant[4] (N. D. Lignite)	8	(11)	56	(1)	12	(3)	0.2	(99)	0.4	(86)

* ppmw means parts per million by weight.
** NA means not available.

Of the five elements considered, mercury appears to be the most volatile. The loss of mercury in the PDU, pilot-plant, and commercial-plant studies ranged from 79% to 99%, whereas the losses of arsenic, boron, and selenium generally fell in the range of 10% to 80%. Lead losses, on the other hand, showed significant variability from one study to the next. In the HYGAS PDU studies, the loss of lead from the feed coal was on the order of 50% for two different coal types. In all other studies, which included the HYGAS pilot-plant gasifier, the Synthane PDU gasifier, and the commercial-scale Lurgi gasifier in Sasol, South Africa, the lead loss was only on the order of 0% to 5%.

Additional data particularly relevant to this study are shown in Table 2. These data are the result of a comprehensive environmental assessment study of the HYGAS process performed by the Institute of Gas Technology under DOE sponsorship.[2] The importance of these data is that the gross behavior of the trace elements as a function of temperature is indicated. The HYGAS gasifier has a number of discrete stages operating at different temperatures and gaseous environments. Differences in the trace element concentration of the chars in each of the stages gives an indication of the flux rates of the trace elements as a function of temperature.

The significant conclusions that can be drawn from these data for the five elements selected for this study are as follows:

- Arsenic volatilization from coal does not appear to be significant until gasification temperatures exceed 1000 K (1341°F). Part of the volatilized arsenic appears to be absorbed or condensed on the char in cooler sections but is not sufficient to reduce losses to less than about 50%.

TABLE 2. TRACE ELEMENT DISPOSITION IN THE HYGAS PILOT PLANT STEAM-OXYGEN GASIFIER USING ROSEBUD SUBBITUMINOUS COAL[2]

Element	Feed Concentration, ppmw	1st Stage Solids (756 K)*	2nd Stage Solids (936 K)	Steam-Oxygen Stage Discharge Solids (1117 K)
		weight fraction retained		
Fe	4900	1.406 ± 0.427**	0.646 ± 0.111**	0.653 ± 0.091**
Ba	755	0.785 ± 0.262	0.843 ± 0.297	0.702 ± 0.105
As	0.52	1.099 ± 0.203	1.372 ± 0.476	0.578 ± 0.221
B	94	0.506 ± 0.088	1.005 ± 0.160	0.628 ± 0.144
Be	0.41	1.008 ± 0.069	1.160 ± 0.013	1.117 ± 0.022
Cl	350	0.403 ± 0.118	0.458 ± 0.119	0.463 ± 0.129
F	36.5	0.624 ± 0.145	0.805 ± 0.202	0.588 ± 0.072
Se	0.42	1.107 ± 0.202	1.033 ± 0.384	0.168 ± 0.020
Tl	0.03	1.564 ± 0.853	0.868 ± 0.403	0.677 ± 0.256
V	9.0	1.126 ± 0.319	1.396 ± 0.321	1.026 ± 0.112
Mn	135	0.803 ± 0.022	1.056 ± 0.016	1.071 ± 0.110
Ni	4.4	1.323 ± 0.228	0.962 ± 0.086	0.854 ± 0.060
Zn	4.0	1.004 ± 0.147	0.681 ± 0.142	1.026 ± 0.334
Li	13.5	1.096 ± 0.137	1.182 ± 0.127	1.070 ± 0.138
Cr	5.4	1.410 ± 0.185	1.212 ± 0.078	1.087 ± 0.161
Cu	7.6	1.383 ± 0.102	1.005 ± 0.040	0.887 ± 0.073
Cd	0.16	1.290 ± 0.134	1.628 ± 0.685	0.356 ± 0.033
Pb	3.9	1.643 ± 0.133	1.248 ± 0.237	1.171 ± 0.175
Mo	3.0	2.554 ± 0.655	1.665 ± 0.513	0.866 ± 0.087
Hg	0.05	0.085 ± 0.041	0.082 ± 0.049	0.186 ± 0.092

* Number in parenthesis is the average operating temperature of stage.
** Standard deviations based on five or more analyses of solids from the same bed at different times.

- Boron appears to be removed from the coal at relatively low temperatures (<750 K, 891°F). Further volatilization appears to occur at higher temperatures but is retained in the char by absorption or condensation on chars in a cooler section (second stage) of the gasifier.

- Selenium does not appear to be volatilized from the char until temperatures in excess of 1000 K (1341°F) are reached. Little, if any, absorption of the volatilized selenium seems to occur in the cooler sections.

- Lead volatilization begins at temperatures in excess of 1000 K (1341°F) but appears to be nearly quantitatively retained by the chars by condensation or absorption on chars in the cooler stages.

- Mercury is volatilized from the coal at temperatures less than 750 K, (891°F).

Although these conclusions are based on HYGAS data, the trace elements are expected to behave in a similar manner in the Lurgi and Koppers-Totzek processes, because of similar reducing environments.

3. PROJECTED TRACE ELEMENT BEHAVIOR IN COAL GASIFICATION ENVIRONMENTS

In this study, predictions on the speciation and concentration of the selected trace elements in raw gasifier product gas have relied heavily upon the fact that the chemical environments existing in coal gasification processes are similar. Although operating temperatures of gasification processes range from 489 K (60°F) to 1811 K (2800°F) and operating pressures range from atmospheric to 10.4 MPa (1500 psig), the environment is generally reducing with H_2, CO, CO_2, and H_2O being the major chemical constituents. Minor constituents such as H_2S, HCl, and NH_3 are also found in most gasification processes, being formed from elemental impurities in the feed coal under the reducing conditions. Some gasification processes (for example, HYGAS, Lurgi, and BI-GAS) also produce large amounts of methane and minor amounts of heavier hydrocarbons such as benzene and tars, but in this study the formation of organometallic compounds was not considered.

The persistence of trace elements in quenched gasifier product gas is directly related to the chemical form of the trace element. Relatively few trace-element-containing substances are volatile at temperatures of 300 K (80°F) or less. The fact that these trace elements are removed from the coal during gasification suggests that either the original chemical form of the element is volatile under gasification conditions or that the trace element has been transformed by chemical reaction. If the trace element is simply distilled from the coal in its original form, recovery in one of the condensate streams from the gas quenching operation should be highly probable. Therefore, a chemical transformation of the trace element into a volatile form is expected to be required if the trace element is to persist in the quenched gasifier product gas.

The chemical reactions that a specific trace element might undergo in a coal gasifier to become volatile are relatively few. Because the environment is generally reducing, two reaction paths that might lead to significant volatilization are simple reduction to the elemental state or reaction with H_2 to form a hydride. The minor constituents, H_2S and HCl, could also play an important role in trace element volatilization. Sulfides and chlorides of the elements are often more volatile than either the oxides or elemental forms of the elements.

With this background, models were developed based on available literature data on the behavior of the trace elements in question under conditions similar to those expected in coal gasification processes. Unfortunately, much of the data, particularly kinetic data, needed to develop accurate models of trace element behavior are not available, and, in most cases, assumptions based on kinetic theory were necessary.

3.1. Arsenic Behavior

The average concentration of arsenic in coal is 14 ppmw, with a maximum value of 93 ppmw and a minimum of 0.5 ppmw.[5] The major form of volatile arsenic in coal has been determined to be arsenopyrite (FeAsS).[6] This was deduced by Duck and Himus in solubility experiments.

Arsenopyrite properties and behavior have been studied by many investigators because of its association with gold-containing ores.[7-11] Zhuchkov[7] studied the behavior of arsenopyrite in an inert gas atmosphere. At elevated temperatures, the arsenopyrite decomposed to form pyrrhotite (FeS) and metallic arsenic. Below 823 K (1021°F) the decomposition was slow. Above 1023 K (1381°F) decomposition proceeded rapidly. Zviadaze, et al.,[8] also studied the decomposition of FeAsS and found metallic arsenic and pyrrhotite as the products. They found the rate to be independent of particle size with an activation energy of 133.9 kJ/mol. Barton[9] performed a thermochemical study of the iron-arsenic-sulfur system. From his study the free energies of formation in Table 3 were determined. Strathdee and Pidgeon[10] studied the thermochemistry of arsenopyrite by measuring the vapor pressure of As_4 and As_2S_3 as a function of the temperature. Results were not reproducible but were reasonably close to the calculated values based on Barton's data. Lukesh[11] also decomposed arsenopyrite and determined arsenic and pyrrhotite to be the products. Based on this information it would appear that arsenopyrite can readily transform into arsenic and pyrrhotite in a gasification process.

TABLE 3. FREE ENERGIES OF FORMATION FOR IRON-ARSENIC-SULFUR SYSTEM[9]

Compound	ΔG_f°, kJ/mol
As_2S_2 (low realgar)	-201.25 + 0.172T*
As_2S_3 (low orpiment)	-288.70 + 0.249T
As_2S_3 (high orpiment)	-288.28 + 0.249T
Fe_2As	-4.60 - 0.054T
FeAs	-17.57 - 0.35T
$FeAs_2$ (loellingate)	-43.30 - 0.030T
FeAsS	-169.45 + 0.068T

* T = temperature, K

Thermodynamic data for other arsenic-containing compounds are provided in Table 4. These data indicate that in typical coal gasification environments, the most stable forms of arsenic from a thermodynamic standpoint are $As_4(g)$, $As_2(g)$, and $AsH_3(g)$. Production of $As_4(g)$ and $As_2(g)$ from the elemental arsenic produced by the decomposition as FeAsS would appear to be straightforward. However, the conversion of arsenic to arsine requires reaction with hydrogen, which may or may not be kinetically controlled under gasification conditions.

A review of the literature produced no information on the kinetics of formation of arsine from hydrogen and arsenic. The normal preparation of AsH_3 is by reaction of AlAs or Na_3As with water[12] or by reaction of $NaBH_4$ with $AsCl_3$ in water at a pH between 8 and 10 and temperatures between 278 and 313 K

TABLE 4. FREE ENERGIES OF FORMATION OF ARSENIC-CONTAINING COMPOUNDS[17]
(Basis: Elements in Their Standard State at Temperature of Interest)

Compound	ΔG_f°, kJ/mol			
	600 K	800 K	1000 K	1200 K
$As_2(g)$	+121.04	+89.87	+59.54	+30.04
$As_4(g)$	+41.84	+12.55	-17.15	-46.86
FeAsS	-128.03	-114.89	-101.25	-87.61
$FeAs_2$ (loellingate)	-61.13	-67.07	-73.01	-78.95
FeAs	-38.66	-45.69	-52.72	-59.75
Fe_2As	-41.42	-48.12	-58.99	-69.87
As_2S_3 (high orpiment)	-139.16	-89.45	-39.75	-9.96
As_2S_3 (low orpiment)	-139.08	-89.20	-39.33	-10.54
As_2S_3 (low realgar)	-98.32	-64.02	-29.71	-4.60
$AsH_3(g)$	+74.81	+81.67	+89.96	+98.32
$As_2O_3(g)$	-488.69	-466.52	-443.50	-420.91
$As_2O_3(s)$	-497.90	-446.85	-396.60	-344.34
$As_2O_3(1)$	-499.99	-461.08	-423.00	-384.93

(40° and 104°F).[13] However, arsine decomposition has been studied by Kedyarkin and Zorin[14] and Tamara.[15] At temperatures between 573 and 707 K (571° and 813°F), Kedyarkin and Zorin determined that arsine decomposition is first order with respect to arsine concentration and has an activation energy of 213 kJ/mol and a pre-exponential rate constant of $6.8 \times 10^{11} s^{-1}$. Tamara determined that the activation energy for arsine decomposition was only 97.1 kJ/mol, but these studies were conducted in the presence of As and Sb films that behaved as catalysts.

If one uses the findings of Kedyarkin and Zorin, assumes that chars have no catalytic activity, and applies the law of microscopic reversibility,[16] one can derive an expression for the rate of formation of arsine from elemental arsenic. The expression is —

$$\frac{d\{AsH_3\}}{dt} = 5.22 \times 10^7 \exp(-27{,}483/T)\{As_4\}^{1/4}\{H_2\}^{3/2} \qquad (2)$$

where time (t) is expressed in seconds, temperature (T) is degrees Kelvin, and the concentrations are in mol/m^3.

Using this expression and calculating a probable concentration for As_4 in a typical coal gasifier gas stream, it can be shown that at temperatures greater than 900 K (1160°F) this reaction is sufficiently fast that thermodynamic equilibrium between the As_4, H_2, and AsH_3 should prevail.

3.2. Selenium Behavior

Selenium is known to exist in U.S. coals at concentrations between 0.45 and 7.7 ppmw.[5] Evidence suggests that most of this selenium is initially present as selenopyrite, FeSeS. In coal combustion, selenium is released as elemental selenium. Approximately 68% is incorporated into fly ash, while the

remainder is lost to the atmosphere. It is therefore assumed that the FeSeS decomposes into FeS and Se(s) at elevated temperatures similar to FeAsS. Solid selenium then vaporizes as $Se_2(g)$.

Under reducing conditions, however, H_2Se is the thermodynamically preferred form.[18] Conversion of $Se_2(g)$ to H_2Se may proceed in coal gasification processes but the rate of this reaction has not been reported in the literature. Hydrogen selenide is prepared in the laboratory by hydrolysis, by the action of dilute acids on selenides of metals Na, K, and Fe, and by the direct reaction of selenium with nascent hydrogen. When nascent hydrogen acts on heated amorphous selenium, the selenium is transformed into the gray modification of H_2Se.[19]

The rate of H_2Se formation in coal gasifiers has been estimated assuming the reaction path by which H_2Se is produced from $Se_2(g)$ and hydrogen takes place in two steps —

$$Se_2 + H \rightarrow HSe + Se \tag{3}$$

$$HSe + H_2 \rightarrow H_2Se + H \tag{4}$$

and that the rate for the initial hydrogenation of $Se_2(g)$ has the Arrhenius form —

$$\frac{-d\{Se_2\}}{dt} = Ae^{[-\Delta E/RT]}\{Se_2\}\{H\} \tag{5}$$

Both of these reactions are abstraction reactions for which empirical relationships have been established between the activation energy and the heat of reaction.[20] For exothermic abstraction reactions, the energy of activation is related to the heat evolved, Q, by the equation —

$$\Delta E(kJ/mol) = 48.116 - 0.25Q \tag{6}$$

whereas for endothermic abstraction reactions it has been found that the energy of activation is closely approximated by —

$$\Delta E(kJ/mol) = 48.116 + 0.75Q \tag{7}$$

The heat evolved in the reaction of Se_2 with H is 56.601 kJ/mol; therefore, the activation energy for this reaction is estimated to be 33.965 kJ/mol. By collision theory, the pre-exponential rate constant, A, is limited to values of $10^{10} m^3 mol^{-1} s^{-1}$ for second-order reactions. Therefore, the rate of reaction of Se_2 with atomic hydrogen is expected to be approximately given by the expression —

$$\frac{-d\{Se_2\}}{dt} = 5.6 \times 10^{10} \exp(-4085.5/T)\{Se_2\}\{H\} \tag{8}$$

where time (t) is expressed in seconds, temperature (T) is degrees Kelvin, and the concentrations are in mol/m^3. Furthermore, if atomic hydrogen is assumed to be in thermodynamic equilibrium with diatomic hydrogen at all times under gasification conditions, then the above expression can be rewritten as —

$$\frac{-d\{Se_2\}}{dt} = 5.6 \times 10^{14} \exp(-34{,}333/T)\{Se_2\}\{H_2\}^{1/2} \qquad (9)$$

where time (t) is expressed in seconds, temperature (T) is degrees Kelvin, and the concentrations are in mol/m^3. For the approximate levels of Se_2 and H_2 expected in coal gasifiers, this expression predicts that the reaction between Se_2 and atomic hydrogen should proceed rapidly at temperatures in excess of 950 K (1250°F). Based on similar assumptions, it can be shown that the reaction between HSe and H_2 proceeds more rapidly than the reaction between Se_2 and H at all temperatures. Therefore, the reaction between Se_2 and H (Equation 3) is expected to control the formation of H_2Se.

3.3. Boron Behavior

Boron is present in U.S. coals at concentrations between 2 and 224 ppmw with an average concentration of 67 ppmw.[5] Evidence suggests that most of the boron is chelated.[21] Chelated boron, when treated with hydrogen at high temperatures, produces BH_3.[22] However, boric acid, $B(OH)_3$, is the thermodynamically preferred form in coal gasification environments based on available free energy data (Table 5).

TABLE 5. FREE ENERGIES OF FORMATION OF BORON-CONTAINING COMPOUNDS[17]

Compound	ΔG_f°, kJ/mol			
	600 K	900 K	1200 K	1800 K
$BH_3(g)$	117.403	126.901	137.863	161.670
$B_2H_6(g)$	148.532	309.744	272.044	396.099
$BH_3CO(g)$	-69.986	-34.334	3.644	91.504
$B(OH)_3(g)$	-860.230	-782.826	-717.556	-572.371
B(g)	466.516	421.329	376.560	288.194

Conversion of borane, BH_3, to $B(OH)_3$ should be extremely rapid under gasification conditions. The hydrolysis of diborane, B_2H_6, to boric acid and hydrogen has long been used for quantitative analysis of diborane in gas mixtures. The mechanism for this reaction has been postulated as[23] —

$$B_2H_6 \rightleftharpoons 2BH_3 \qquad (10)$$

$$BH_3 + H_2O \rightleftharpoons BH_3 * H_2O \rightarrow BH_2OH + H_2 \qquad (11)$$

$$BH_2OH + H_2O \rightleftharpoons BH_2OH * H_2O \rightarrow BH(OH)_2 + H_2 \qquad (12)$$

$$BH(OH)_2 + H_2O \rightleftharpoons BH(OH)_2 * H_2O \rightarrow B(OH)_3 + H_2 \qquad (13)$$

The rate controlling step is believed to be the initial attack of H_2O on BH_3 (Equation 11). The kinetics of this reaction has been estimated to be[23] —

$$\frac{-d\{BH_3\}}{dt} = 1.9 \times 10^5 \exp(-3020/T)\{BH_3\}\{H_2O\} \qquad (14)$$

where time (t) is expressed in seconds, temperature (T) is degrees Kelvin, and the concentrations are in mol/m^3. This kinetic expression indicates that the conversion of borane to boric acid proceeds quite rapidly, even at temperatures as low as 200 K (—100°F).

3.4. Lead Behavior

Limited information is available in the literature on the reaction chemistry of lead under conditions expected in coal gasification processes. Therefore, only thermodynamic considerations were used in developing a model to predict the speciation of lead in raw product gas streams from coal gasifiers. Relevant thermodynamic data for some potential lead-containing compounds are shown in Table 6.

TABLE 6. FREE ENERGIES OF FORMATION OF LEAD-CONTAINING COMPOUNDS[24]

Compound	ΔG_f°, kJ/mol
PbS(g)	82.473 - 0.06772T*
PbS(s)	-132.076 + 0.06511T
$PbCO_3$(s)	-671.135 + 0.23943T
$PbCl_2$(s)	-328.611 + 0.09540T
$PbCl_2$(g)	-192.214 - 0.01632T
PbO(g)	58.928 - 0.05195T
PbO(s)	-216.836 + 0.09682T
Pb(g)	185.230 - 0.09185T
Pb(s)	0.0

* T = temperature, K.

Based on thermodynamic calculations, the stable solid form of lead in gasification atmospheres is PbS. However, at high temperatures, a number of reactions could theoretically result in the significant volatilization of lead. These are —

$$PbS(s) \rightleftharpoons PbS(g) \qquad (15)$$

$$PbS(s) + 2HCl(g) \rightleftharpoons PbCl_2(g) + H_2S(g) \qquad (16)$$

$$PbS(s) + H_2(g) \rightleftharpoons Pb(g) + H_2S(g) \qquad (17)$$

$$PbS(s) + H_2O(g) \rightleftharpoons PbO(g) + H_2S(g) \qquad (18)$$

At moderate temperatures, however, most of these lead compounds were found to have very low vapor pressures. In coal gasification processes where a

significant temperature gradient exists between the exiting fuel gas stream and the maximum gasification temperature, precipitation of these species on the coal is quite likely and must be taken into account. This is the probable cause of the disparity between the HYGAS PDU data and data obtained from larger scale plants. The HYGAS PDU operated isothermally at temperatures above 1100 K (1600°F). Therefore, the volatile lead-containing compounds formed in the gasifier were able to escape with the raw product gases.

3.5. Mercury Behavior

The concentration of mercury in U.S. coal ranges from 0.02 ppmw to 1.60 ppmw with an average concentration of 0.2 ppmw.[5] As with lead, little information is available about specific reaction chemistry relevant to coal gasification environments; therefore, thermodynamic considerations were employed.

Under all typical conditions expected in coal gasifiers, elemental mercury vapor, Hg(g), was determined to be the thermodynamically preferred form. Other mercury-containing species considered were HgS(g), $HgCl_2$(g), and HgF_2(g). Therefore, in our subsequent disposition calculations, volatilized mercury was assumed to be elemental.

4. PROJECTED SPECIATION OF THE TRACE ELEMENTS IN GASIFIER PRODUCT GAS STREAMS

For this study, a subbituminous coal feed was assumed for all three processes. The trace element concentration of the subbituminous coal, however, was assumed to vary, corresponding to the maximum, minimum, and average concentrations found in U.S. coals. The purpose of this variation was to examine its effect on speciation.

The coal, oxygen, and steam feed rates and the resulting production rates for both the major and minor constituents for these three processes are shown in Table 7 for equivalent SNG production rates. As can be seen, the difference in operating characteristics of these three processes results in differing feed requirements and product gas distributions. The HYGAS process produces the largest amount of methane in the gasifier and uses the least amount of coal and oxygen. The Koppers-Totzek process produces negligible amounts of methane, consumes the largest quantity of oxygen because of its high operating temperature, but requires the least amount of steam.

The projections on the speciation of the volatile forms of the trace elements assumed that the composition of the gas was constant throughout the gasifier. This simplification was necessary since information on the variation in gas composition with location within the gasifier is generally not available. The temperature history of the coal and gases was, however, taken into account to the extent possible.

4.1. Projected Distribution of Arsenic

In Section 3.1, it was shown that the volatile forms of arsenic in coal gasifier raw product gas streams are likely to be elemental arsenic (As_2, As_4) and arsine (AsH_3). Furthermore, the interconversion between these two forms was postulated to be described by the kinetic expression —

$$\frac{d\{AsH_3\}}{dt} = 5.22 \times 10^7 \exp(-27{,}483/T)\{As_4\}^{1/4}\{H_2\}^{3/2} \qquad (19)$$

where time (t) is expressed in seconds, temperature (T) is degrees Kelvin, and the concentrations are in mol/m^3. This kinetic expression indicates that the distribution of arsenic is equilibrium controlled at temperatures greater than 900 K (1160°F). Data on the global behavior of arsenic contained in coals from the HYGAS pilot plant indicated that significant volatilization does not occur until the coal reaches a temperature greater than 1000 K (1340°F). Therefore, the concentration of arsine and elemental arsenic in the raw

TABLE 7. PROJECTED PERFORMANCE FOR THE HYGAS (STEAM-OXYGEN), CONVENTIONAL LURGI, AND KOPPERS-TOTZEK PROCESSES USING SUBBITUMINOUS COAL AND PRODUCING 3.052 GJ/s (250 Billion Btu/d) OF EQUIVALENT SNG

Process	HYGAS	Lurgi	Koppers-Totzek
Gasifier Feed, kg/s			
Coal	183.7525	210.2312	210.3535
Carbon	109.9272	106.3011	119.3596
Hydrogen	7.1937	6.6804	8.9230
Nitrogen	1.3094	1.8995	2.1226
Sulfur	1.5034	2.2954	1.3887
Oxygen	26.8350	20.6111	27.7174
Chlorine	0.0450	0.0634	0.0712
Ash	14.8887	20.4529	46.5527
Moisture	22.0501	51.9270	4.2057
Oxygen	34.5947	51.2889	136.4731
Steam	197.8692	234.1028	28.5984
Raw Product Gas, mol/s			
H_2O	7593.0	11,410.1	1310.4
H_2	2662.5	5318.7	4972.0
CO	1501.8	1960.1	8879.6
CO_2	3472.4	4012.8	1064.6
N_2	4.9	12.7	85.3
CH_4	2221.1	1448.2	0
C_2-C_5	114.7	111.4	0
H_2S	40.3	64.9	42.3
COS	1.6	3.8	3.0
NH_3	59.8	79.5	0.5
HCN	1.0	0.06	0.3
HCl	0.4	0.4	2.0
Phenols (as C_6H_5OH)	8.3	10.8	0
Fatty Acids, kg/s	0	0.4097	0

product gas was assumed to be equivalent to that predicted by assuming an equilibrium temperature of 900 K (1160°F).

In moderate temperature processes [maximum temperature less than 1255 K (1800°F)] it appears that roughly 50% of the feed arsenic is removed from the coal. This constraint was assumed for the HYGAS and Lurgi processes. The Koppers-Totzek process, however, operates under slagging conditions (>1800 K, 2780°F). For this process, it was assumed that nearly quantitative removal of arsenic occurs.

The projected concentrations of arsine and elemental arsenic from the three processes are shown in Table 8. The major conclusions that can be drawn from these projections are 1) the fraction of the arsenic removed from the coal that forms arsine increases with increasing operating pressure and 2) the fraction forming arsine increases with decreasing arsenic concentration although the total quantity of arsine decreases.

4.2. Projected Distribution of Selenium

As discussed in Section 3.2, the two selenium-containing compounds expected to be found in raw gasifier product gas are H_2Se and Se_2. Furthermore, the rate of conversion of Se_2 to H_2Se, when the two compounds are far from being in equilibrium, is expected to be described by the kinetic expression —

$$\frac{d\{H_2Se\}}{dt} = 1.1 \times 10^{15} \exp(-34{,}333/T)\{Se_2\}\{H_2\}^{1/2} \qquad (20)$$

where time (t) is expressed in seconds, temperature (T) is degrees Kelvin, and the concentrations are in atmospheres. This kinetic expression indicates that above 950 K (1250°F) the reaction is extremely rapid and thermodynamic equilibrium should prevail. Since selenium is not removed from the coal until temperatures are in excess of 1000 K (1340°F), the relative distribution of H_2Se and Se_2 was assumed to be described by an equilibrium distribution calculated at 950 K (1250°F).

As with arsenic, it was further assumed that only 50% of the total selenium found in the coal was converted to H_2Se and Se_2 in the HYGAS and Lurgi processes. In the Koppers-Totzek process, quantitative removal was assumed because of the slagging conditions.

With these assumptions, it was found that H_2Se should be the major selenium-containing compound in the raw product gas from these three gasification processes. The projected concentrations of H_2Se in commercial-sized versions of these processes are given in Table 9 for feed coals containing 0.45, 2.08, and 7.70 ppmw Se.

4.3. Projected Distribution of Boron

In Section 3.3, it was shown that the major volatile form of boron expected in coal gasifier raw product gas was boric acid, $B(OH)_3$. This is due to the very rapid hydrolysis of borane, BH_3, which is expected to be an intermediate product from the hydrogenation of the chelated boron found in the coal.

The fraction of the boron in the feed coal that ultimately forms boric acid, $B(OH)_3$, is again assumed to be directly related to the maximum operating temperature in the reactor. For the HYGAS and Lurgi processes, 50% conversion was assumed in the calculations while for the Koppers-Totzek process 100% conversion was assumed. With these assumptions, the projected concentrations of

TABLE 8. PROJECTED ARSENIC DISTRIBUTION IN RAW PRODUCT GAS STREAMS FROM THE HYGAS (Steam-Oxygen), LURGI, AND KOPPERS-TOTZEK GASIFIERS

	HYGAS Steam-Oxygen			Lurgi			Koppers-Totzek		
Operating Pressure, kPa (psia)	8167 (1184)			2068 (300)			206.8 (30)		
Hydrogen Partial Pressure, kPa (psia)	1221 (177)			449 (65)			62.9 (9.1)		
Coal Feed, kg/s (tons/h)	183.5 (729)			209.9 (834)			210.2 (835)		
Gasifier Product Gas Flow, mol/s (lb-mol/h)	17,768 (1.41 X 10^5)**			24,462 (1.94 X 10^5)††			15,005 (1.19 X 10^5)††		
Arsenic Volatilization, %	50			50			100		
Arsenic Species	AsH_3	As_4	As_2	AsH_3	As_4	As_2	AsH_3	As_4	As_2
Arsenic Concentration in Feed Coal, ppmw†	Concentration in Raw Product Gas, ppmv*								
93	0.48	1.48	0.005	0.29	1.05	0.009	0.10	3.94	0.097
14	0.28	0.17	0.0018	0.17	0.16	0.0032	0.065	0.58	0.018
0.5	0.034	0.00007	0.00002	0.028	0.00011	0.00008	0.024	0.014	0.0027

* ppmv means parts per million by volume.
† ppmw means parts per million by weight.
** Excluding slurry oil.
†† Excluding water quench sprays.

TABLE 9. PROJECTED SELENIUM DISTRIBUTION IN RAW PRODUCT GAS FROM THE HYGAS, LURGI, AND KOPPERS-TOTZEK GASIFIERS

	HYGAS Steam-Oxygen		Lurgi		Koppers-Totzek	
Operating Pressure, kPa (psia)	8167 (1184)		2068 (300)		206.8 (30)	
Hydrogen Partial Pressure, kPa (psia)	1221 (177)		499 (65)		62.9 (9.1)	
Coal Feed kg/s (tons/h)	183.5 (729)		209.9 (834)		210.2 (835)	
Gasifier Product Gas Flow, mol/s (lb-mol/h)	17,768 (1.41 X 10^5)**		24,462 (1.94 X 10^{-5})††		15,005 (1.19 X 10^5)††	
Selenium Volatilization, %	50		50		100	
Selenium Species	H_2Se	Se_2	H_2Se	Se_2	H_2Se	Se_2
Selenium Concentration in Feed Coal, ppmw†	Concentration in Raw Product Gas, ppmv*					
7.70	0.504	7.5 X 10^{-8}	0.419	9.7 X 10^{-8}	1.370	5.3 X 10^{-6}
2.08	0.135	5.4 X 10^{-9}	0.113	7.0 X 10^{-9}	0.370	3.9 X 10^{-7}
0.45	0.029	2.5 X 10^{-10}	0.024	3.2 X 10^{-10}	0.080	1.8 X 10^{-8}

* ppmv means parts per million by volume.
† ppmw means parts per million by weight.
** Excluding slurry oil.
†† Excluding water quench sprays.

$B(OH)_3$ in the raw product gas from these processes are given in Table 10 for feed coals containing 2, 67, and 224 ppmw boron.

4.4. Projected Distribution of Lead

As mentioned in Section 3.4, limited volatilization of lead is expected in gasification processes where the outlet gas temperature is moderate (>900 K, 1160°F). This is due to the low vapor pressure of lead-containing compounds at these temperatures resulting in precipitation.

Projections on the distribution of the trace amounts of volatile lead-containing compounds in the three gasification processes assumed that 1) the partial pressures of the volatile lead-containing compounds were in thermodynamic equilibrium with PbS when the temperature exceeded 900 K and 2) the lead-containing compounds were in physical equilibrium with their solid form if temperatures were less than 900 K. For the HYGAS and Lurgi processes this meant that as the gas phase approached 900 K, the volatile lead content of the gas was assumed to be equivalent to that predicted from thermodynamics, but as the gases rose further in the gasifier and became cooler a fraction of the lead-containing compounds precipitated on the coal in accordance with their vapor pressure. Since the Koppers-Totzek gasifier operates isothermally at 1800 K, the volatile lead-containing compounds in the hot raw product gas were assumed to be in thermodynamic equilibrium with PbS at this temperature, but as the raw product gas passes through the waste heat boiler where it is cooled to 900 K, the lead-containing compounds precipitate in accordance with their vapor pressure and end-up with the particulate matter entrained from the gasifier. The resulting concentrations of the various volatile lead-containing compounds using these assumptions are given in Table 11 and, as can be seen, the concentrations represent only a small fraction of the total lead contained in the coal.

4.5. Projected Distribution of Mercury

Since the major form of mercury expected in the raw product gas stream from all gasification processes is elemental, the concentration and mass flow rate of elemental mercury in the raw product gas is simply related to the fraction volatilized from the feed coal not adsorbed on entrained particles and the quantity of gas produced per unit mass of coal. Since all data from environmental assessment studies show mercury losses in excess of 80%, it was simply assumed that 100% of the mercury contained in the coal was volatilized regardless of concentration and gasifier operating temperature. The resultant projections on the concentrations of mercury in the raw product gas stream from these processes are given in Table 12 for feed coals containing 0.02, 0.2, and 1.68 ppmw of mercury.

TABLE 10. PROJECTED BORON DISTRIBUTION IN RAW PRODUCT GAS FROM COMMERCIAL-SIZE HYGAS, LURGI, AND KOPPERS-TOTZEK GASIFIERS

	HYGAS Steam-Oxygen	Lurgi	Koppers-Totzek
Operating Pressure, kPa (psia)	8167 (1184)	2068 (300)	206.8 (30)
Coal Feed, kg/s (tons/h)	183.5 (729)	209.9 (834)	210.2 (835)
Gasifier Product Gas Flow, mol/s (lb-mol/h)	17,768 (1.41×10^5)**	24,462 (1.94×10^5)††	15,005 (1.19×10^5)††
Boron Volatilization, %	50	50	100
Boron Species	$B(OH)_3$		
Boron Concentration in Feed Coal, ppmw†	Concentration in Raw Product Gas, ppmv*		
224	106.3	88.3	288.4
67	31.8	26.4	86.3
2	0.95	0.79	2.6

* ppmv means parts per million by volume.
† ppmw means parts per million by weight.
** Excluding slurry oil.
†† Excluding water quench sprays.

TABLE 11. PROJECTED LEAD DISTRIBUTION IN RAW PRODUCT GAS FROM COMMERCIAL SIZE HYGAS, LURGI, AND KOPPERS-TOTZEK GASIFIERS

	HYGAS Steam-Oxygen	Lurgi	Koppers-Totzek
Operating Pressure, kPa (psia)	8167 (1184)	2068 (300)	206.8 (30)
Coal Feed, kg/s (tons/h)	183.5 (729)	209.9 (834)	210.2 (835)
Gasifier Product Gas Flow, mol/s (lb-mol/h)	17,768 (1.41×10^5)**	24,462 (1.94×10^5)††	15,005 (1.19×10^5)††
Lead Concentration in Feed Coal, ppmw*	>1	>1	>1
Lead Species Concentration in Raw Product Gas, ppmv†			
PbS	1.12×10^{-7}	1.49×10^{-8}	9.50×10^{-4}
$PbCl_2$	1.53×10^{-5}	1.79×10^{-5}	1.50×10^{-7}
PbO	3.87×10^{-19}	5.57×10^{-20}	1.24×10^{-10}
Pb	9.57×10^{-10}	1.03×10^{-16}	6.08×10^{-3}
Total	1.54×10^{-5}	1.79×10^{-5}	1.56×10^{-4}

* ppmw means parts per million by weight.
† ppmv means parts per million by volume.
** Excluding slurry oil.
†† Excluding water quench sprays.

TABLE 12. PROJECTED ELEMENTAL MERCURY CONCENTRATIONS IN RAW PRODUCT GAS FROM COMMERCIAL-SIZE HYGAS, LURGI, AND KOPPERS-TOTZEK GASIFIERS

	HYGAS Steam-Oxygen	Lurgi	Koppers-Totzek
Operating Pressure, kPa (psia)	8167 (1184)	2068 (300)	206.8 (30)
Coal Feed kg/s (tons/h)	183.5 (729)	209.9 (834)	210.2 (835)
Gasifier Product Gas Flow, mol/s (lb-mol/h)	17,768 (1.41 X 10^5)**	24,462 (1.94 X 10^5)††	15,005 (1.19 X 10^5)††
Mercury Species	Hg(g)		
Mercury Concentration in Feed Coal, ppmw†	Concentration in Raw Product Gases, ppmv*		
1.68	0.0823	0.0684	0.1030
0.20	0.0103	0.0086	0.0138
0.02	0.0010	0.0009	0.0010

* ppmv means parts per million by volume.
† ppmw means parts per million by weight.
** Excluding slurry oil.
†† Excluding water quench sprays.

5. PROJECTED DISPOSITION OF THE VOLATILE TRACE ELEMENTS IN DOWNSTREAM PROCESSES

A generic processing scheme was assumed in this study to project the disposition of the volatile forms of the selected trace elements. A schematic of the processing scheme is presented in Figure 5.

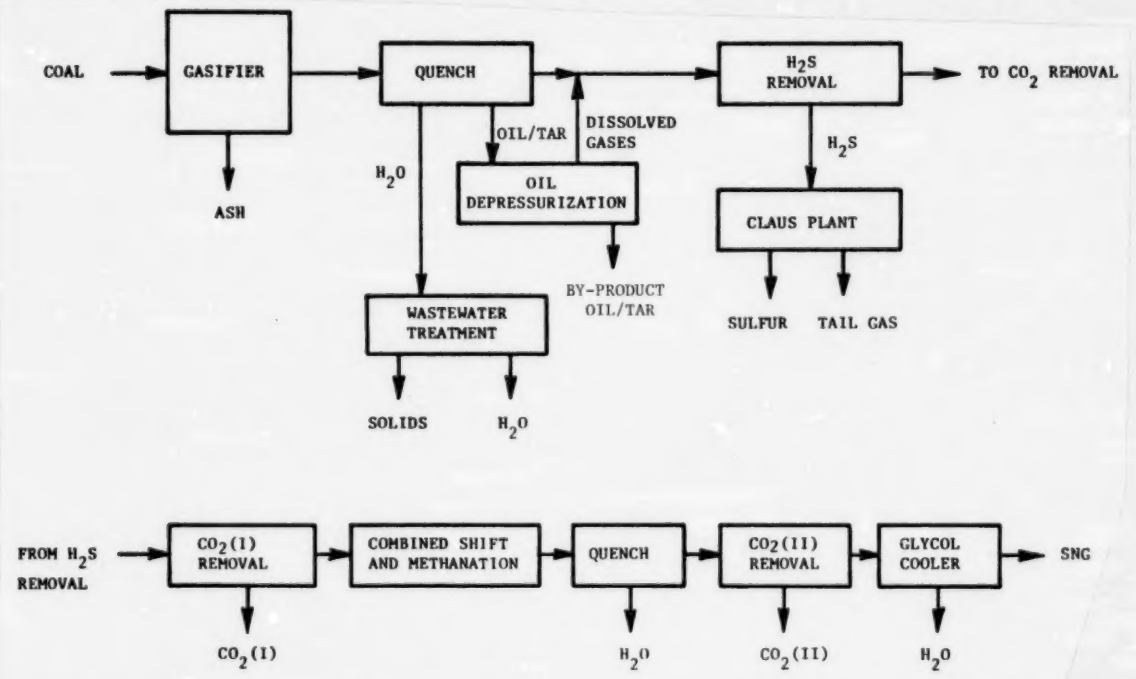

Figure 5. Typical gas processing configuration for producing SNG.

5.1. Description of Processing Scheme

The first step in processing the raw product gas from most coal gasification processes is gas quench. In this process, the raw product gas temperature is generally reduced to approximately 311 to 322 K (100° to 120°F). Condensate recycle with heat exchange is generally used to accomplish the temperature reduction. As a result, the unreacted steam, tars, and most of the light oils are condensed and separated by density differences. If the process is operated at high pressures, the excess condensate and light oils are generally flashed before further treatment and the dissolved gases that are recovered are recompressed into the quenched gas stream.

Excess condensate from the quench operation generally contains dissolved materials such as phenols, ammonia, hydrogen sulfide, hydrogen cyanide, thiocyanate, hydrogen chloride, carbon dioxide, and sparingly soluble organics such as benzene, toluene, and naphthalene. In most coal gasification design studies, this excess condensate is only treated sufficiently to be used as cooling tower makeup. The preferred approach by vendors to treatment of the condensate at this time is —

1. Solvent extraction of the wastewater to recover dissolved organics such as phenols — for example, by the Phenosolvan or Chem-Pro processes

2. Steam stripping of the extracted condensate to remove ammonia and produce an anhydrous ammonia by-product — for example, by the U.S. Steel Phosam-W process

3. Biological treatment of the extracted and stripped condensate for destruction of residual organics and biodegradable inorganics such as cyanide and thiocyanate.

Any dissolved materials remaining in the condensate after this treatment are then either recovered as part of the blowdown from the cooling tower operations or escape the cooling tower as part of the evaporation or drift losses.

The recovered light oils and tars from the quench operations are generally treated as saleable by-products or used as fuel in the process. In the case of the HYGAS® process, the bulk of the recovered oil is recycled to produce an oil-coal slurry that is convenient for pumping coal into a high-pressure reactor.

The quenched gasifier product gas, which is essentially free of water, oil, and tar, is then treated to remove acid-gases. In this process, the acid-gases CO_2 and H_2S are removed from the quenched gasifier product gas using a gas-liquid absorption process. Several commercial processes are available. The most often considered processes are the Norton Company Selexol process, the Lurgi Rectisol process, and the Benfield hot aqueous potassium carbonate process. Several configurations are possible with these processes. The actual choice usually depends upon the composition of the gas being treated.

A two-stage configuration has been chosen by most process designers. The first stage removes the H_2S and a fraction of the CO_2. The second stage removes the remainder of the CO_2. This set-up has the advantage that the gas stream derived from regeneration of the solvent from the first absorber is much higher in H_2S-content than would be obtainable if bulk absorption of H_2S and CO_2 were employed. This permits the use of the more energy efficient Claus process for conversion of the H_2S into elemental sulfur, which can be sold as a by-product. Additionally, if the CO_2 recovered by the second absorber is environmentally acceptable, it may be discharged directly into the atmosphere after preheating to provide buoyancy for proper dispersion.

The major constituents remaining in the gas after acid-gas removal are H_2, CO, and CH_4. Trace amounts of other compounds may be present but the only

ones of concern to the process are those containing sulfur. The next gas processing step involves a sulfur-sensitive catalyst. A feed gas containing less than 0.1 ppmv* of sulfur-containing compounds is required for an acceptable catalyst life. This specification is generally met by heating the fuel gas to a temperature above 553 K (500°F) and then passing the gas through a bed of zinc oxide where the zinc oxide reacts with the sulfur-containing gases to produce zinc sulfide.

The sulfur-sensitive catalytic processing step after zinc oxide treatment has been termed the combined shift-methanation process. In this process, a suitable quantity of steam is added to the fuel gas to avoid carbon deposition and to provide a sufficient source of hydrogen for the reactions. The two reactions occurring in this process step are 1) the water gas shift reaction —

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (21)$$

and 2) the methanation reaction —

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (22)$$

A feed gas temperature of 533 K (500°F) is generally sufficient to initiate this reaction and the exothermic nature of the methanation reaction is able to carry the reactions to completion.

The product gas from the combined shift-methanation process is essentially methane, carbon dioxide, and steam. The bulk of the steam is removed by quenching the gas, and carbon dioxide is removed by another acid-gas removal process leaving only methane (SNG).

The only steps remaining before the methane is delivered into the gas transmission lines is compression to pipeline pressure and sufficient moisture removal to ensure a dew point of the gas of less than 233 K (-40°F). Moisture removal is generally accomplished using an ethylene glycol absorption process.

5.2. Projected Disposition of the Trace Elements in the Quench System

A simplified quench system configuration was assumed for this study. A schematic of the quench system is shown in Figure 6. In this system the raw gas is quenched to 316 K (110°F) at the operating pressure of the gasifier by recycle of the aqueous condensate after heat recovery.

Projections on the disposition of the various trace-element-containing compounds assumed that all phases were in thermodynamic equilibrium at 316 K (110°F) and the operating pressure of the gasifier.

The Peng-Robinson equation of state[25] was used to project the equilibrium distribution of the major components between the vapor and oil phases. Edward's correlation[26] was used to project the equilibrium distribution of the

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* ppmv means parts per million by volume.

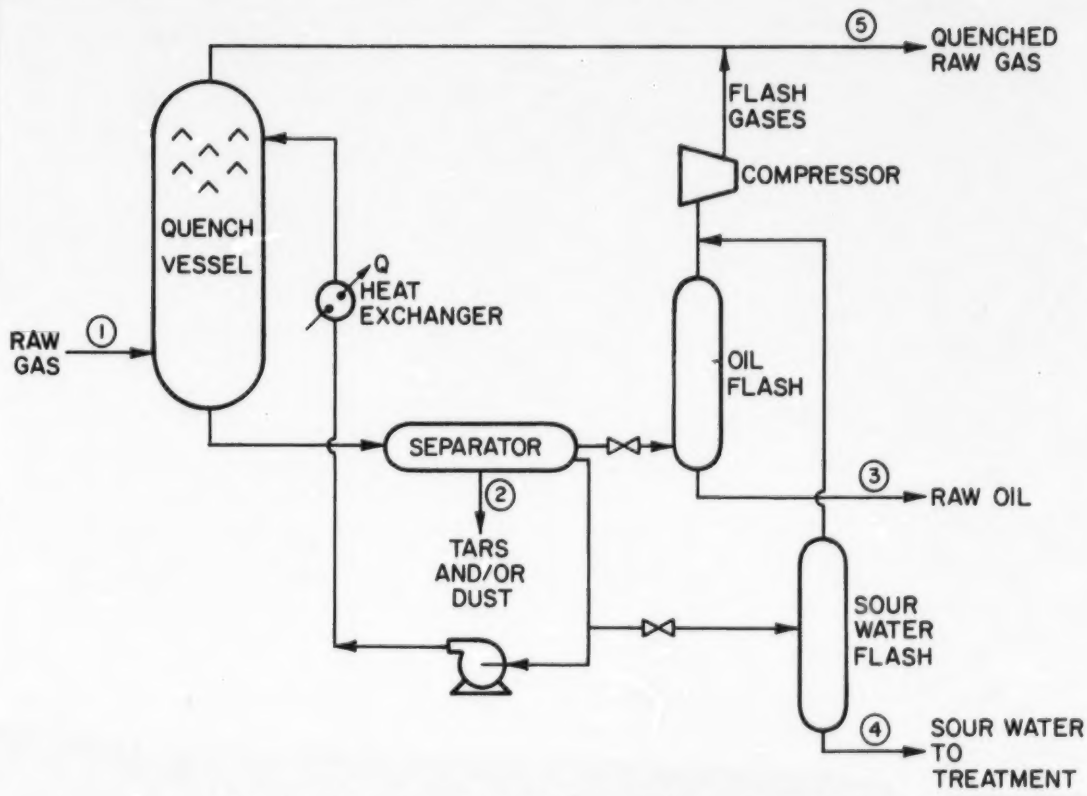

Figure 6. Generic raw fuel gas quench system.

weak electrolytes, CO_2, H_2S, NH_3, and HCN, between the vapor and aqueous phases and Henry's law constants[27] were used to project the equilibrium distribution of the remaining major constituents between the vapor and aqueous phases. For the minor and trace constituents, Raoult's law[28] was applied to estimate solubilities in the oil phase, and estimated Henry's law constants were used to estimate the solubility in the aqueous phase. For constituents other than NH_3, H_2S, and CO_2 that may form electrolytes in the aqueous phase (for example, H_2Se, AsH_3, and lead-containing constituents), pK_a values (acid dissociation constants) reported by Freiser and Fernando[29] and Naumov, et al.,[30] were used to estimate the degree of reaction.

The results of these calculations project the following behavior for the trace-element-containing compounds in the generic quench operation.

- Greater than 90% of the arsine remains with the quenched fuel gas stream reporting to the acid-gas removal plant for all three processes.

- Elemental arsenic is recovered in the aromatic oil of the HYGAS process and the oil/tar by-product of the Lurgi process. In the case of the Koppers-Totzek process, where no oil or tar is produced, the arsenic precipitates during quench and leaves as suspended solids in one of the condensate streams.

- The lead-containing compounds are converted to insoluble lead sulfide in the quench operation of all three processes due to the presence of dissolved H_2S in the sour water. The lead should leave the system as suspended solids.

- Boric acid is highly soluble in aqueous systems and should be quantitatively recovered in the aqueous condensate stream in all three processes.

- Hydrogen selenide is partially removed by the aqueous condensate. More than 75% of the H_2Se remains in the quenched gas stream of the Koppers-Totzek process but less than 10% of the H_2Se remains in the quenched fuel gas of the Lurgi and HYGAS processes.

- Mercury remains in the quenched fuel gas in all three processes.

Only AsH_3, Hg, and H_2Se remain in the quenched fuel gas stream. The projected range of concentration for these constituents in the three processes is shown in Table 13 for the range of trace element concentrations used in this study. The projections show that all three processes are expected to have similar levels of AsH_3 and Hg in the quenched fuel gas stream. Only in the case of H_2Se is any difference noted. The Koppers-Totzek process is expected to have considerably more H_2Se than either the HYGAS or Lurgi processes. This is due to the predicted acidic nature of the condensate from the Koppers-Totzek process, which suppresses the solubility of H_2Se in the sour water.

TABLE 13. PROJECTED CONCENTRATION RANGE FOR THE TRACE ELEMENTS IN THE QUENCHED GAS STREAM

	HYGAS Steam-Oxygen	Lurgi	Koppers-Totzek
Quenched Fuel Gas Flow, mol/s	10,172	13,122	11,645
Constituent	Concentration, ppmv		
AsH_3	0.06-0.60	0.05-0.50	0.03-0.13
H_2Se	0.003-0.06	0.003-0.05	0.08-1.36
Hg	0.002-0.14	0.002-0.13	0.002-0.13

Projections on the concentrations of dissolved forms of the trace constituents in the sour water from the three processes are shown in Table 14. Comparison of the projections shows that the sour water from the three processes is expected to have only ppb quantities of dissolved arsenic, mercury, and lead. The projected concentrations of boron and selenium are significantly higher. The projected concentrations of boron and selenium in the Koppers-Totzek sour water are probably much higher than will be experienced in an actual plant, as the quench water spray used to reduce the temperature of the raw fuel gas is not included.

TABLE 14. PROJECTED CONCENTRATION RANGE FOR THE TRACE ELEMENTS IN SOUR WATER FROM RAW GAS QUENCH

	HYGAS Steam-Oxygen	Lurgi	Koppers-Totzek
Sour Water Production, kg/s	136.41	204.11	6.05*
Element	Concentration, ppmw		
As	0.002-0.03	0.02-0.2	0.0002-0.001
B	1-150	1-100	70-8000
Hg	0.003-0.02	<0.008	<0.0008
Pb	<0.0001	<0.0001	<0.0001
Se	0.3-5	0.2-4	4-60

* Excludes water spray for partial quench; projected concentrations uncertain.

Neither the dissolved boron nor the selenium in the sour water is expected to be removed by conventional waste water treatment techniques. Boric acid is very soluble in water and is difficult to either extract or strip. Hydrogen selenide, H_2Se is a stronger acid than H_2S and is difficult to remove unless the sour water is acidified. Therefore, these two elements are projected to be predominantly recovered in the blowdowns or brines from the various evaporation systems that might be employed in the plant (for example, cooling tower, solar evaporation ponds).

The projected concentrations of the selected trace elements in the product oil from the HYGAS process and the Lurgi process are shown in Table 15.

TABLE 15. PROJECTED CONCENTRATION RANGE FOR THE TRACE ELEMENTS IN THE OIL PRODUCED IN THE HYGAS AND LURGI PROCESSES

	HYGAS Steam-Oxygen	Lurgi
Oil Production Rate, kg/s	9.46	4.40
Element	Concentration, ppmw	
As	1-900	1-2000
B	NP*	NP
Hg	0.0003-0.02	<0.008
Pb	NP	NP
Se	0.0005-0.008	0.0002-0.004

*NP means no projection.

Arsenic is the only trace element in this study that has the potential to significantly contaminate the oil produced in these two processes. This is

due to the solubility of elemental arsenic in aromatic solvents. However, because of the low vapor pressure of elemental arsenic most of the arsenic could be removed from the oil by a distillation step. The concentrations of boron and lead in the oil could not be determined because of the lack of partition coefficient data for these substances.

5.3. Projected Disposition in the Gas Cleanup Sections

Arsine, hydrogen selenide, and mercury are the only forms of the trace elements projected to remain in the quenched raw fuel gas in the three gasification processes. The next step in the treatment of this gas is acid-gas removal where it is assumed that H_2S is removed and converted to elemental sulfur, and CO_2 is removed, treated, and discharged into the atmosphere.

Although many acid-gas removal processes are commercially available for removing H_2S and CO_2 from fuel gases, the three processes most often chosen for conceptual plant designs have been the Selexol process, the Rectisol process, and the Benfield process.

The Selexol and Rectisol processes use physical-type solvents and are generally applied to gas streams at pressures above 1000 kPa (150 psia). The Selexol process uses a mixture of the dimethylethers of polyethylene-glycol as the solvent and is generally designed to operate at temperatures around 278 K (40°F). The Rectisol process uses methanol as the solvent and operates around 247 K (-15°F).

The Benfield process uses a chemical-type solvent that is a mixture of potassium carbonate and water. This mixture is alkaline and reversibly reacts with the acid-gases. This process is generally applied to low-pressure streams where the Selexol and Rectisol processes are uneconomical. The operating temperature for this process is around 383 K (230°F).

For this study, the Selexol process was chosen for use in the HYGAS process. The Rectisol process was chosen for the Lurgi process and the Benfield process was chosen for the Koppers-Totzek process. The operating configurations chosen for the acid-gas removal processes are shown in Figures 7 through 9. In each case the first stage of the acid-gas removal system was designed to quantitatively remove H_2S and produce an H_2S-rich acid-gas stream containing at least 15% H_2S, which is an acceptable H_2S concentration for feeding a Claus sulfur production plant. The remaining CO_2 is then removed in the second-stage, treated if necessary, and discharged into the atmosphere.

Since no information is available regarding the solubility of AsH_3, H_2Se, and Hg in these solvents, estimates were necessary. As mentioned previously, H_2Se is more acidic than H_2S and also has a lower vapor pressure. Therefore, quantitative recovery in the first-stage of each acid-gas removal process is expected with the H_2Se exiting the process in the H_2S-rich-acid-gas stream. Arsine, AsH_3, is less polar than ammonia, NH_3, and has a boiling point of 210 K (-80°F), which is intermediate between ethane and propane. Since the solubility of CO_2 in the Selexol and Rectisol solvents is also intermediate between ethane and propane, the disposition of AsH_3 is expected to parallel that of CO_2. In the case of the Benfield process where a chemical reaction is

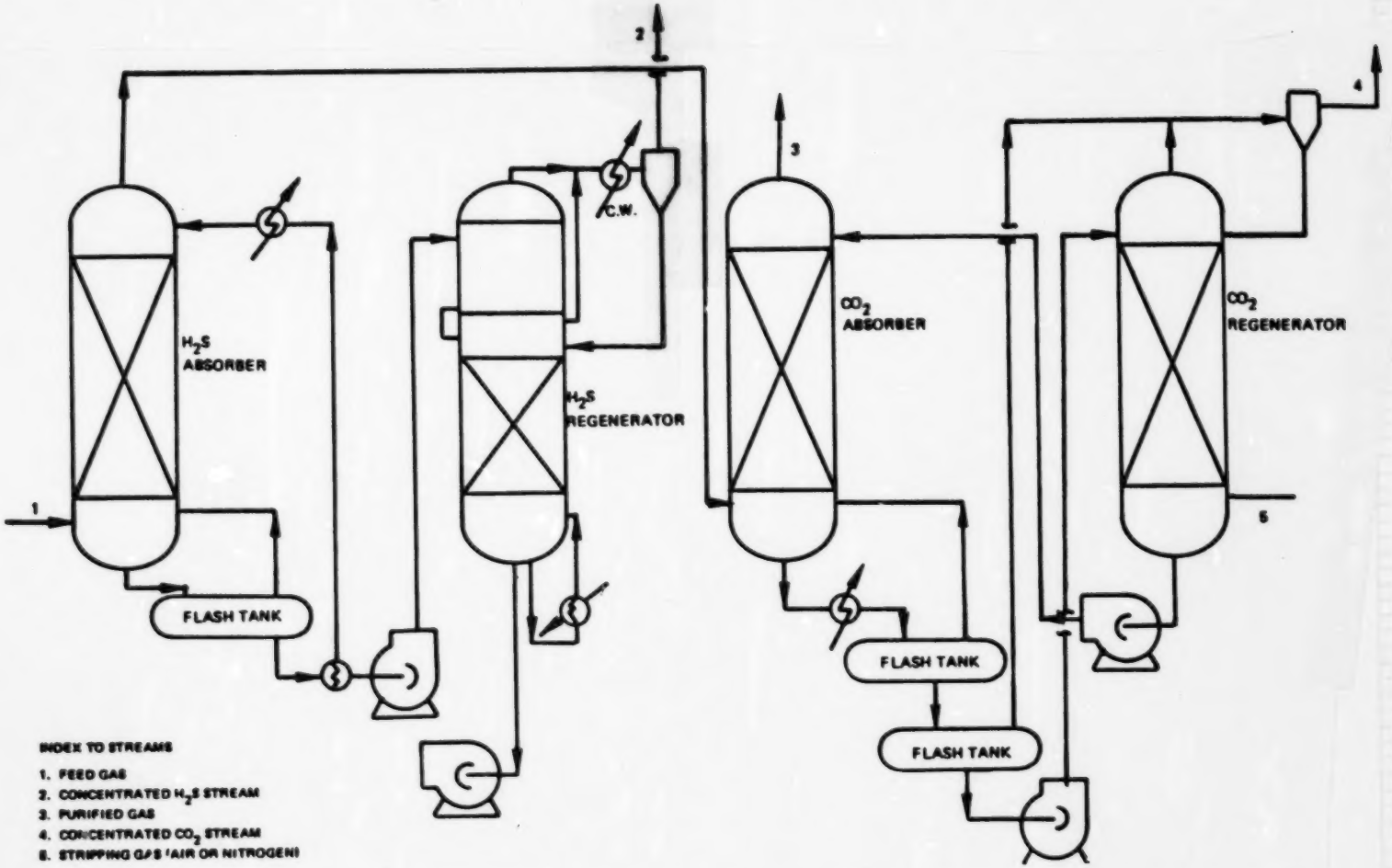

Figure 7. Selexol acid-gas removal process.[31]

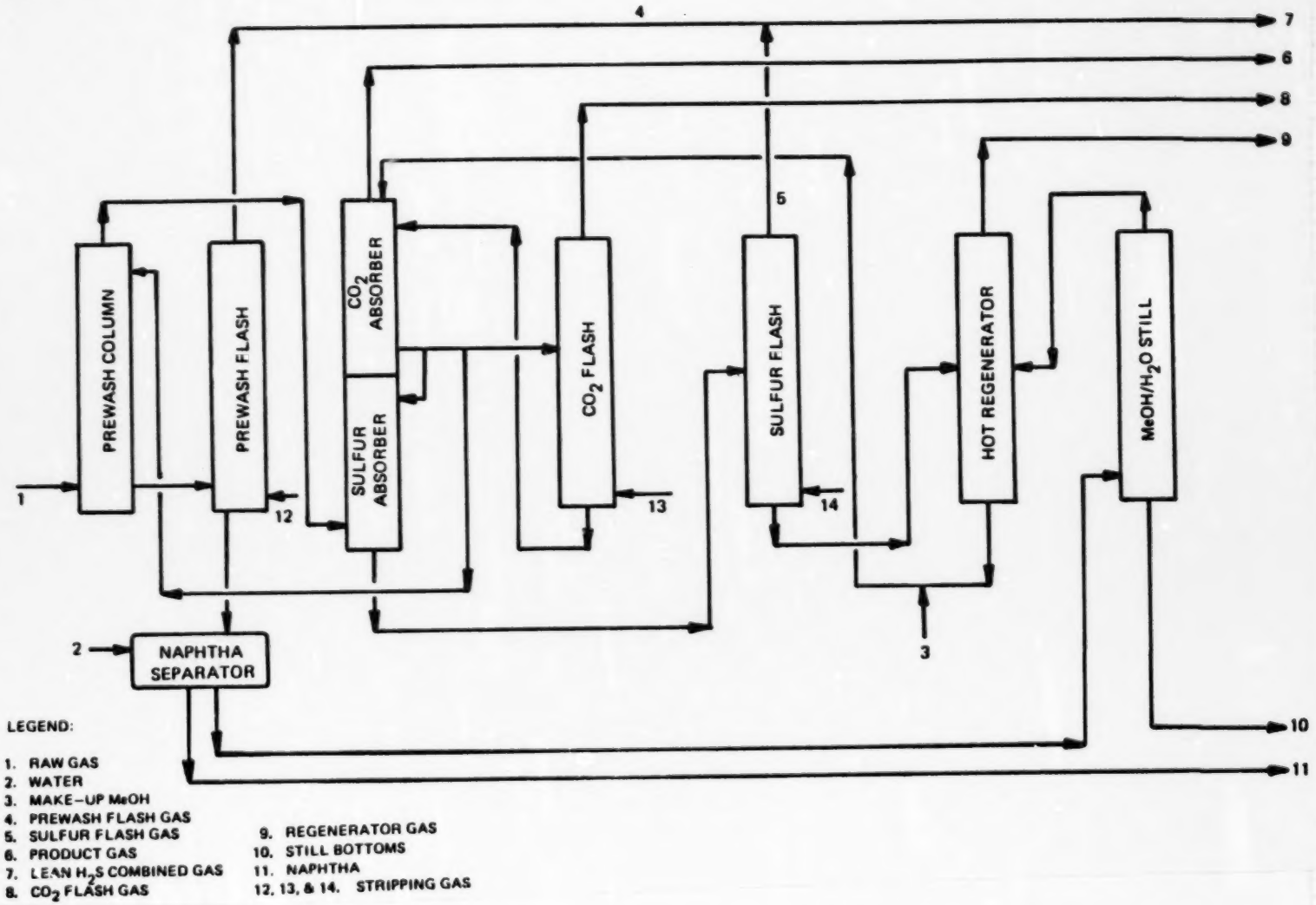

Figure 8. Rectisol acid-gas removal process.[31]

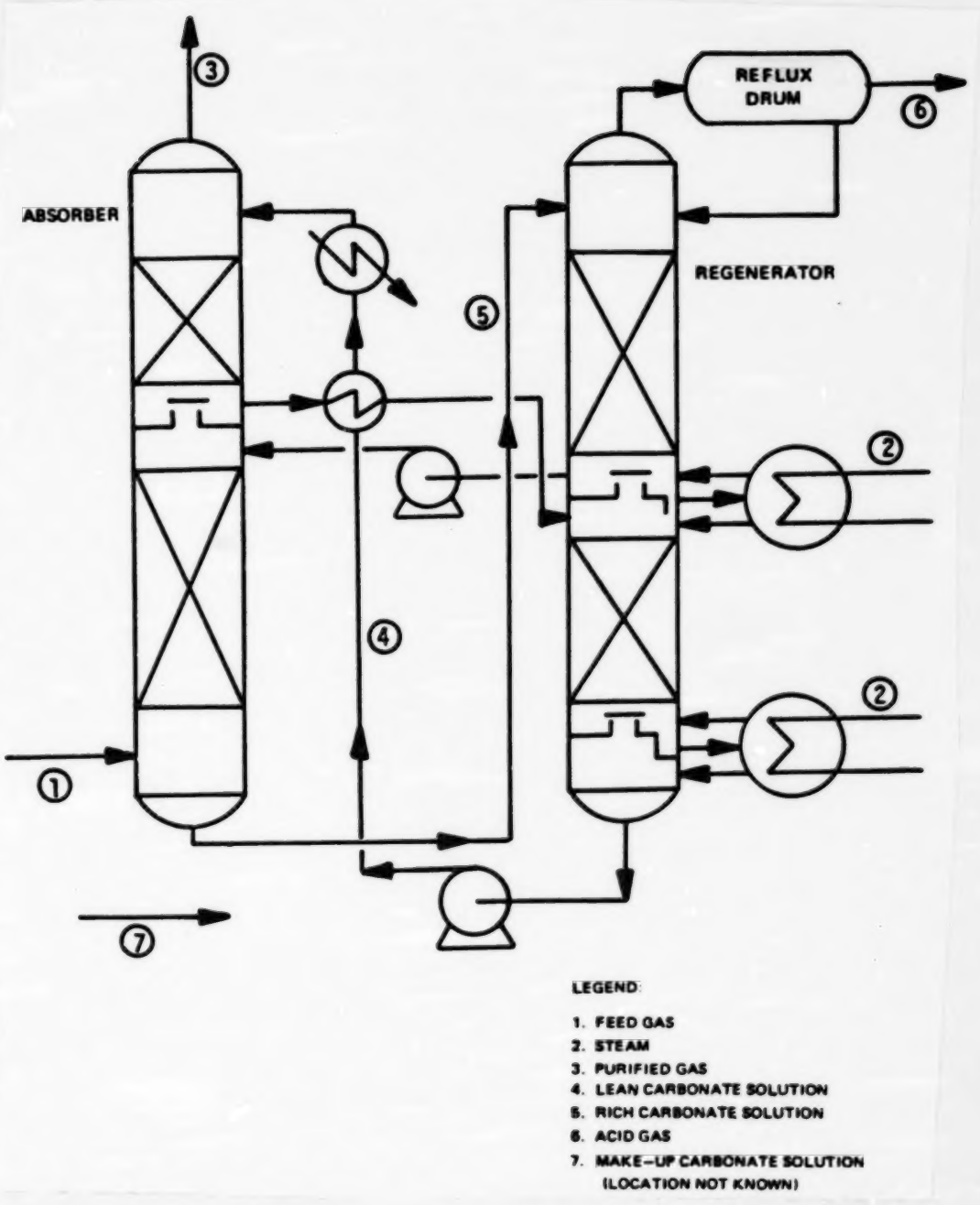

Figure 9. Benfield acid-gas removal process.[31]

involved in the removal of the acid-gases, the removal of AsH_3 is expected to be negligible. The Henry's law constant for AsH_3 is roughly 3037 MPa (30,000 atmospheres) at 394 K.[32]

The disposition of mercury in the acid-gas removal processes is the most difficult to predict because of its non-ideal behavior. At saturated conditions the solubility of mercury in water is reported to be 0.02 to 0.03 g/kg H_2O at 303 K (30°C).[33] The vapor pressure of mercury at 303 K (85°F) is 3.7×10^{-7} MPa (3.7×10^{-6} atmospheres).[34] This indicates a Henry's law constant for mercury in water of roughly 0.2 MPa (2 atmospheres). In organic solvents, the Henry's law constant is expected to be less than this value. The Henry's law constant for H_2S in the Selexol solvent is roughly 0.5 MPa (5 atmospheres) at 300 K (80°F).[35] In the Rectisol solvent, the Henry's law constant for H_2S is roughly 2 MPa (20 atmospheres) at 273 K (32°F).[36] Therefore, assuming the mass transfer rate is adequate for the mercury to approach physical equilibrium with the organic solvents, nearly quantitative removal is expected in the first stage of both the Selexol and Rectisol processes.

Nearly quantitative removal of mercury in the first stage of the Benfield process may also be achieved. Solvent flow rate for the first stage is twice that needed to remove the mercury assuming that the Henry's law constant for mercury at 383 K (230°F) is still on the order of 0.14 MPa (1.4 atmospheres). This is considered to be a reasonable assumption since the Henry's law constant for solutes in water generally decreases with an increase in temperature.

Based on these assumptions, the projected disposition of AsH_3 H_2Se, and Hg in the three processes is shown in Table 16. If these projections are reasonable, the only compound that appears to be of any environmental significance at this stage of the process is arsine, which is expected to appear in the CO_2-rich acid-gas stream of the Selexol and Rectisol processes. This stream is emitted into the atmosphere after treatment. The treatment to be used on this stream is ill-defined at this stage of development of the coal gasification processes. Thermal incineration followed by SO_2 removal is one option. Arsine would be expected to be converted to particulate As_2O_3 by an incineration process.

Another outcome of these projections that may be of concern to process developers is the concentration of the trace-element-containing compounds in the H_2S-rich acid gas. If these compounds are recovered in the by-product elemental sulfur, their concentrations could exceed that found in Frasch sulfur[37] and may make it a less desirable feedstock for sulfuric acid production. These contaminants can be removed in sulfuric acid plants but make the process more expensive. A comparison of the possible concentrations of the trace elements in the product sulfur and the concentration of these elements in typical Frasch sulfur is shown in Table 17.

The only trace element, of the five being considered in this study, that is projected to remain in the treated fuel gas is arsine and that is only anticipated to occur for the Benfield process. This arsine, however, is expected to decompose into elemental arsenic and hydrogen in either the zinc

TABLE 16. PROJECTED DISPOSITION OF ARSINE, HYDROGEN SELENIDE, AND MERCURY IN THE ACID-GAS REMOVAL SECTION

	Process		
	HYGAS Selexol	Lurgi Rectisol	Koppers-Totzek Benfield
	H_2S-Rich Acid Gas		
Flow Rate, mol/s	268.7	432.7	282.0
AsH_3, ppmv	0.15-2.07	0.14-1.39	<0.001
H_2Se, ppmv	0.11-2.27	0.09-1.52	3.3-56.2
Hg, ppmv	0.08-5.30	0.06-3.94	0.08-5.37
	CO_2-Rich Acid Gas		
Flow Rate, mol/s	3244.0	3645.0	824.9
AsH_3, ppmv	0.18-2.43	0.16-1.63	0.001
H_2Se, ppmv	<0.001	<0.001	<0.001
Hg, ppmv	<0.001	<0.001	<0.001
	Treated Fuel Gas		
Flow Rate, mol/s	6659	9044.3	10,538
AsH_3, ppmv	<0.001	<0.001	0.03-0.14
H_2Se, ppmv	<0.001	<0.001	<0.001
Hg, ppmv	<0.001	<0.001	<0.001

TABLE 17. COMPARISON OF POTENTIAL TRACE ELEMENT CONCENTRATION IN BY-PRODUCT SULFUR FROM COAL GASIFICATION PROCESSES WITH FRASCH SULFUR

	Process			
	Frasch Sulfur	HYGAS Selexol	Lurgi Rectisol	Koppers-Totzek Benfield
Element	ppmw			
Se	<2	0.8-37.3	1.5-25	54-924
As	<0.25	2.3-32.3	2.2-21.7	<0.01
Hg	ND*	3.3-221	2.5-165	3.3-224

* Not Determined

oxide guard chambers or the combined-shift methanation section where the fuel gas is catalytically converted to SNG (methane). The elemental arsenic should remain as a vapor in these processes but should precipitate during subsequent quench of the fuel gas stream. As a result, none of the five trace elements considered in this study is expected to remain in the product SNG of any of the three gasification processes.

6. SUMMARY

The projected dispositions of the selected trace elements in the major process streams produced in coal gasification plants are summarized in Tables 18 through 22. The flow rates in the tables correspond to plants producing 3.052 GJ/s (250 billion Btu/d) of SNG and reflect the range of feed concentrations expected for these trace elements. The major conclusions that can be derived from this study are summarized below.

TABLE 18. PROJECTED DISPOSITION OF ARSENIC IN THE HYGAS, LURGI, AND KOPPERS-TOTZEK PROCESSES

	HYGAS	Lurgi	Koppers-Totzek
	Feed Streams, kg/d		
Coal	8-1500	9-1700	9-1700
	Product Streams, kg/d		
Solids			
Char/Ash	4-750	4.5-850	0
Filtered Solids	0	0	9-1700
Liquids			
Oil/Tar	0.8-700	0.4-740	0
Sour Water	0.2-0.3	0.3-3.0	<0.001
Gases			
H_2S-Rich Acid Gas	0.3-3.6	0.4-3.9	<0.02
CO_2-Rich Acid Gas	3.8-50	3.8-38	<0.07
SNG	0	0	0

6.1. Summary of Arsenic Behavior

Volatilization of arsenic from coal is expected to range from 50% for moderate temperature (<1280 K) gasification processes to approximately 100% for slagging processes (>1400 K). Between 5% and 10% of the volatilized arsenic is expected to appear as arsine, AsH_3, in the raw fuel gas produced by the gasifier for coals containing high levels of arsenic (>50 ppm). While between 70% and 80% of the volatilized arsenic is expected to appear as arsine for coals containing low levels of arsenic (<1 ppm), the balance of the volatilized arsenic is expected to be elemental forms, As_4 and As_2.

TABLE 19. PROJECTED DISPOSITION OF BORON IN THE HYGAS, LURGI, AND KOPPERS-TOTZEK PROCESSES

	HYGAS	Lurgi	Koppers-Totzek
	Feed Streams, kg/d		
Coal	32-3550	36-4060	36-4060
	Product Streams, kg/d		
Solids			
Char/Ash	16-1775	18-2030	0
Filtered Solids	0	0	0
Liquids			
Oil/Tar	0	0	0
Sour Water	16-1775	18-2030	36-4060
Gases			
H_2S-Rich Acid Gas	0	0	0
CO_2-Rich Acid Gas	0	0	0
SNG	0	0	0

TABLE 20. PROJECTED DISPOSITION OF MERCURY IN THE HYGAS, LURGI, AND KOPPERS-TOTZEK PROCESSES

	HYGAS	Lurgi	Koppers-Totzek
	Feed Streams, kg/d		
Coal	0.4-25	0.4-29	0.4-29
	Product Streams, kg/d		
Solids			
Char/Ash	0	0	0
Filtered Solids	0	0	0
Liquids			
Oil/Tar	0	0	0
Sour Water	<0.001	<0.002	<0.001
Gases			
H_2S-Rich Acid Gas	0.4-25	0.4-29	0.4-29
CO_2-Rich Acid Gas	<0.05	<0.05	<0.03
SNG	0	0	0

TABLE 21. PROJECTED DISPOSITION OF LEAD IN THE HYGAS, LURGI, AND KOPPERS-TOTZEK PROCESSES

	HYGAS	Lurgi	Koppers-Totzek
	Feed Streams, kg/d		
Coal	63-3460	72-3950	73-3960
	Product Streams, kg/d		
Solids			
Char/Ash	63-3460	72-3950	73-3960*
Filtered Solids	<0.005	<0.008	<0.05
Liquids			
Oil/Tar	0	0	0
Sour Water	<0.0002	<0.0002	<0.0001
Gases			
H_2S-Rich Acid Gas	0	0	0
CO_2-Rich Acid Gas	0	0	0
SNG	0	0	0

* K-T gasifier residue includes entrained slag recovered in waste heat boiler.

TABLE 22. PROJECTED DISPOSITION OF SELENIUM IN THE HYGAS, LURGI, AND KOPPERS-TOTZEK PROCESSES

	HYGAS	Lurgi	Koppers-Totzek
	Feed Streams, kg/d		
Coal	7.1-122	8.2-140	8.2-140
	Product Streams, kg/d		
Solids			
Char/Ash	3.5-66	4.1-70	0
Filtered Solids	0	0	0
Liquids			
Oil/Tar	<0.005	<0.005	0
Sour Water	3.5-59	3.8-65	2.0-31
Gases			
H_2S-Rich Acid Gas	0.2-4.2	0.3-4.5	6.3-108
CO_2-Rich Acid Gas	<0.02	<0.02	<0.01
SNG	0	0	0

The elemental forms of arsenic have low vapor pressures under quenching conditions (~300 K) and precipitate in this operation. However, elemental arsenic is soluble in aromatic solvents. Therefore, for those processes producing oil and/or tar, the elemental arsenic may appear in these products. Arsine, on the other hand, is not appreciably removed by aqueous condensates or aromatic oils after these liquids have been flashed to atmospheric pressure. Therefore, arsine is expected to remain with the quenched fuel gas stream.

Based on the vapor pressure of arsine in relationship to hydrocarbon gases, arsine is expected to be nearly quantitatively removed in acid-gas removal processes using physical solvents such as in the Selexol and Rectisol processes, and its disposition is expected to parallel that of CO_2. If the projections are correct, the concentration of arsine in the CO_2-rich acid gas may be of environmental concern. The projected range is from 0.2 ppmv for low-arsenic-containing coal to around 2 ppmv for high-arsenic-containing coals. This arsenic may also contaminate the elemental sulfur produced in these plants.

In chemical-solvent-type acid-gas removal processes such as the Benfield process, arsine is not expected to be removed. Therefore, the arsine appears in the treated gas fed to a combined-shift-methanation system where it is expected to decompose into elemental arsenic and hydrogen. This catalytically converted fuel gas is then quenched, and the elemental arsenic will precipitate as in the previous quench system.

6.2. Summary of Boron Behavior

As with arsenic, volatilization of boron from coal is expected to range from about 50% for moderate temperature gasification processes to about 100% for slagging processes. In the case of boron, however, only one predominant form is expected in the raw fuel gas. This is boric acid, $B(OH)_3$. Boric acid is extremely soluble in aqueous solutions and should be essentially quantitatively recovered in the raw fuel gas quench systems of a gasification plant.

6.3. Summary of Mercury Behavior

Mercury is expected to be nearly quantitatively volatilized from coal in all the coal gasification processes studied in this program. It is expected to be in its elemental form in the raw fuel gas streams from these processes. Its removal in the quench system is expected to be minimal due to flashing gases back into the quenched fuel gas stream.

Although elemental mercury is not particularly soluble in organic or aqueous solvents, the flow rates of the acid-gas removal solvent used for recovery of H_2S is projected to be sufficient for quantitative recovery of the mercury. As a result, mercury is projected to be predominantly recovered in the H_2S-rich acid-gas feed to elemental sulfur production facilities in most coal gasification processes. As with arsenic, contamination of the by-product elemental sulfur may result.

6.4. Summary of Lead Behavior

Based on the theoretical projection of this study, less than 0.01% of the lead contained in coal is expected to appear in the raw fuel gas of the three gasification processes. Although many lead-containing compounds are volatile at the highest temperatures employed in coal gasification processes, they exhibit very small vapor pressures at the exit temperatures of the three gasification processes examined in this study. In the case of K-T process, this lower temperature includes the effect of the initial quench, and the lead condensed on the carry-over ash is considered to leave the system with the total slag. As a consequence, the bulk of the lead remains in the ash and char recovered from the gasification step.

6.5. Summary of Selenium Behavior

Selenium appears to behave much the same way as sulfur in coal during gasification. Most of it is removed from the coal during gasification and appears as hydrogen selenide, H_2Se, in the raw fuel gas. Hydrogen selenide is more acidic than H_2S, however, and more of it is recovered in quench operations than H_2S. In the case of the HYGAS and Lurgi processes, which operate at elevated pressures, between 90% and 95% of the H_2Se is expected to be recovered in the sour water. In the Koppers-Totzek process, which operates at lower pressures and whose sour water is more acidic, recovery of H_2Se is expected to be lower, about 22%.

The balance of the H_2Se in all three processes is expected to be recovered in the first stage of the acid-gas removal system and be part of the H_2S-rich acid-gas stream. As in the case of arsenic and mercury, this selenium could contaminate the by-product elemental sulfur.

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